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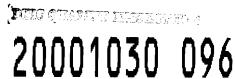
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# Surface Chemistry, Vibrational Dynamics, and Structural Stability of Metallic Interfaces

## AFOSR-F49620-96-1-0084

Final Technical Report for March 1, 1996 - October 31, 1999

Submitted by: Steven J. Sibener

Department of Chemistry and The James Franck Institute The University of Chicago, 5640 South Ellis Avenue Chicago, Illinois 60637

	ontents
<u>1.</u>	Cover Sheet (Form 298)1
2.	Objectives
3.	Status of Effort4
4.	Accomplishments/New Findings5
	4.1 Ultra-High-Vacuum STM Imaging and Scattering Studies of Metals
	in Oxidizing Environments
	4.2 Atomic Oxygen Interactions with Clean and Adsorbate Covered Metallic Surfaces
	4.3 Metallic Oxidation Using Energetic Oxidants: High Kinetic Energy Molecular Oxygen
	4.4 Influence of Surface Stress in Oxidation/Corrosion Chemistry of Al, Al-2024-T3, NiAl
	4.5 Formation of High-Density and Highly-Ordered Water Layers on (1x1)-O-Rh(111)
	4.6 The Effect of Cluster Formation on Mass Separation in Binary Molecular Beams
	4.7 Adsorbates on Stepped/Kinked Metallic Interfaces - Nanostructures
	4.8 Polymer Thin Film Coatings
	4.9 Multiphonon Energy Transfer in Gas-Surface Collisions
	4.10 Surface Ordering Kinetics of Metallic Alloys
	4.11 Surface Chemistry
5.	Personnel Supported and Associated with this Program
6.	Publications (19 Manuscripts)
7.	Interactions/Transitions1/
8.	New Discoveries, Inventions, or Patent Disclosures
a	Honors/Awards 18

2. Objectives

This research initiative explored the interactions of neutral particle, electron, and optical beams with well-characterized single crystal surfaces. These studies were motivated by the desire to understand and control surface reactions, such as surface oxidation/corrosion, the technological need to characterize the physical properties of thin films and surfaces, and the desire to understand how energy and momentum are exchanged at the surface of a material when it is subjected to gas-surface collisions, electron-surface collisions, optical illumination, or chemical reaction. Experiments aimed at determining the surface phonon dispersion relations for a variety of clean and adsorbate covered systems played an important role in this program. Such measurements are crucial for elucidating how the force constants at the surface differ from those characteristic of the bulk for a given material, and how adsorption of atomic and molecular species modify the force constants, and hence structural stability, in the vicinity of the surface. Especial attention was also given to elucidating which surface vibrational modes actively participate in collision induced energy exchange, and determining under which energy regimes single phonon, multi-phonon, and electron-hole pair processes are significant energy absorption mechanisms. Structural studies employing helium atom scattering and STM also formed a key part of this program. Our efforts have concentrated on a variety of structural and dynamical research projects which have improved our understanding of clean, alloyed, oxidized, and stepped metallic interfaces. Major advances have occurred, for example, in our understanding of the forces which are present at steps, a useful paradigm for examining the properties of extended surface defects; major advances have also occurred in the area of metallic oxidation, including oxide nucleation, structural change, and interfacial kinetic processes which have direct bearing on metallic corrosion. Measurements involving elastic and inelastic helium atom scattering, inelastic electron scattering, molecular beam reactive scattering at interfaces, and scanning probe microscopy formed the experimental basis of this work, while lattice dynamics, molecular dynamics, and scattering calculations supported these investigations. We have established air/electrochemical/and ultra-high-vacuum STM/AFM imaging instrumentation which significantly enhanced our research capabilities in the area of atomic-level surface chemistry, including new detailed studies of polymer thin film coatings.

### 3. Status of Effort

This program utilizes three incisive scattering instruments to examine the structure, stability, and chemical reactivity of metallic surfaces. Moreover, to complement these capabilities, we have designed and built a new laboratory for ultra-high vacuum STM and air/electrochemical STM/AFM microscopy; these new microscopes became fully operational during the past grant period. We have continued our pioneering experiments which involve the interaction of atomic oxygen beams with metallic surfaces. We have shown that novel high density oxygen overlayers can be formed, and that surface-to-bulk oxygen incorporation proceeds much more rapidly at moderate temperatures, when atomic rather than molecular oxygen is the oxidant. We have also shown that water layers adsorbed on the high-density oxygen overlayer are highly ordered and form new ice structures. Work on the initial stages of oxidation of smooth and stepped surfaces of Ni has also continued, most recently in our new UHV-STM facility. New results confirm that the surface chemistry and stability regimes for different structures are sensitive to the extent of oxygen dissolved in the sample and, hence, the oxidative history of the material. We have initiated experiments which are delineating how incident kinetic energy influences the key nucleation step for metallic oxidation. Measurements of surface phonons continue to provide information on the chemical bonding interactions which govern the structure and stability of metallic surfaces, especially at extended surface defects. Major advances have also occurred in the area of metallic oxidation, including oxide nucleation, kinetics and thermodynamics of oxygen-driven structural changes, and synergistic effects involving electrons which significantly modify metallic oxidation kinetics. Research on the surface structure and stability of metallic alloys is also underway. As an offshoot from our beam-surface experiments, we have discovered enhanced methods of mass separation in skimmed supersonic flows. Finally, our new scanning probe microscopy effort is now underway. In liquid and electrochemical environments we are exploring the corrosion behavior of Al, NiAl, and Al alloys, including the influence that applied stress has on surface reactivity. Finally, we are also examining the microscopic details of how the morphology of polymer thin films evolve during annealing, including single defect dynamics.

4. Accomplishments/New Findings

The past 4 years have been a <u>remarkable period of scientific discovery</u>, personnel development, instrumentation development, and, as shown below, highly productive publication in leading journals.

During 2000 2 projects, polymer annuli and nanostructure templating, were **COVER STORIES** in *Langmuir* and the *J. of Physical Chemistry B*, respectively.

Perhaps the best way to summarize this productivity is to give brief synopses followed by the publication references and publication abstracts for different projects.

Please note that most recently we have succeeded in making real-time elevated-temperature STM "movies" of atomically resolved dynamics during metallic oxidation. This latter work is being readied for publication at this time.

Finally, please also note that additional findings related to this, our "core" AFOSR grant, can be found in the Final Technical Report for AASERT grant F49620-96-1-0268, which has as its "parent" grant, now elapsed, AFOSR-F49620-93-1-0423.

Table of Contents for this Section

- 4.1 Ultra-High-Vacuum STM Imaging and Scattering Studies of Metals in Oxidizing Environments
- 4.2 Atomic Oxygen Interactions with Clean and Adsorbate Covered Metallic Surfaces
- 4.3 Metallic Oxidation Using Energetic Oxidants: High Kinetic Energy Molecular Oxygen
- 4.4 Influence of Surface Stress in Oxidation/Corrosion Chemistry of Al, Al-2024-T3, NiAl
- 4.5 Formation of High-Density and Highly-Ordered Water Layers on (1x1)-O-Rh(111)
- 4.6 The Effect of Cluster Formation on Mass Separation in Binary Molecular Beams
- 4.7 Adsorbates on Stepped/Kinked Metallic Interfaces Nanostructures
- 4.8 Polymer Thin Film Coatings
- 4.9 Multiphonon Energy Transfer in Gas-Surface Collisions
- 4.10 Surface Ordering Kinetics of Metallic Alloys
- 4.11 Surface Chemistry

\*NOTE: Following the research descriptions for each of the above listed 11 sections are the paper references and abstracts of the relevant manuscripts. The paper numbers refer to the publications section of this report.

4.1 Ultra-High-Vacuum STM Imaging and Scattering Studies of Metals in Oxidizing Environments

It has been a most productive period for our new UHV-STM research effort. Accomplishments have come both in instrumentation development/completion as well as in scientific discovery. Graduate student Tom Pearl has completed the last innovation for our new UHV-STM, namely the ability to do imaging at elevated temperatures in real-time during chemical reactions. He has obtained, for example, atomically resolved images of Ni(111), as well as of oxygen islands on these surfaces which reveal the crucial role that step defects play in nucleating such structures. He has also now imaged stepped metals in real-time during oxidation, as well as atomically-resolved studies of electron stimulated oxidation. Movies have recently been made of step facetting during surface oxidation. Such imaging is beginning to reveal how step meandering contributes to the doubling mechanism, i.e., whether one should view this as a "zippering" process in which one point of contact (pinning connection) between adjacent steps greatly

accelerates step merging. Our work has attracted wide-spread attention, with several theory groups going after the electronic, structural, and kinetic aspects of our work. The reader is referred to recent publications from our group for more background material on this topic. See, for example: Reconstruction Kinetics of a Stepped Metallic Surface: Step Doubling and Singling of Ni(977) Induced by Low Oxygen Coverage, L. Niu, D.D. Koleske, D.J. Gaspar, S.F. King and S.J. Sibener, Surface Science 356, 144 (1996). Our ability to conduct these experiments is largely due to the high degree of vibration isolation he has achieved, and the implementation of exceptionally quiet electronics for this microscope. In this arena Tom has continued to work quite closely with Topometrix Corporation, giving them valuable feedback on needed improvements in their software package for STM control. The software for tunneling spectroscopy (CITS) has recently been validated. Please note that the AASERT student has taken this project from its inception to operational status: he designed the layout for our new STM laboratory, designed the custom-built and vibrationally isolated ultra-high vacuum STM chamber, and successfully integrated all required sub-systems to produce a working UHV-STM with atomic resolution.

Paper #13. Proximity Heater for the Elevated Temperature *In Situ* Vacuum Scanning Tunneling Microscopy of Metal Surfaces, T.P. Pearl and S.J. Sibener, Rev. Sci. Instrum. <u>71</u>, 124-127 (2000).

The design and application of a radiant heater assembly for elevated temperature scanning tunneling microscopy (STM) in ultra-high vacuum (UHV) is presented. The proximity heater is a non-invasive modification to an existing commercial room-temperature microscope and is capable of radiatively heating samples up to 650 K in situ. Imaging at higher temperatures should be readily accessible with other microscope construction designs. It is demonstrated that this heater is well suited for enabling an STM to capture surface morphological transformations such as the motion of atomic steps on metal surfaces at elevated temperature. Various design issues and solutions related to variable temperature UHV-STM are also discussed. We believe the approach described to be general in nature, offering a direct route to adapting UHV-STM designs for elevated temperature imaging.

Paper #1. Reconstruction Kinetics of a Stepped Metallic Surface: Step Doubling and Singling of Ni(977) Induced by Low Oxygen Coverage, L. Niu, D. D. Koleske, D. J. Gaspar, S. F. King and S. J. Sibener, Surf. Sci. 356, 144 (1996).

Helium atom diffraction has been used to study the reconstruction kinetics of a stepped metallic surface, Ni(977), which sequentially undergoes step-doubling and singling upon dosing with low coverages of oxygen. Over the temperature range 390 - 470 K it was found that less than 2% of a monolayer of oxygen was sufficient to transform the initially prepared single-stepped surface to a new steady state having a double-stepped structure. The thermal range over which the doubled phase exists extends to higher temperatures when more oxygen is present. At low oxygen exposures this doubled interface reverts to the single-stepped surface above 470K. Singling can also be driven by more extensive levels of oxygen adsorption. The kinetics of the step-doubling transformation which occurs below 470 K was determined to be second order with respect to single-step density, while, for temperatures above 470 K, step-singling followed first order kinetics with respect to the double-step density. Oxygen atoms adsorbed at step edges play a crucial role in these transformations. Arrhenius analysis is used to extract energetics for the step-doubling and singling reconstructions. These results delineate the sequence of mechanistic stages which occur during the initial stages of oxidation of a stepped metallic interface which precede the onset of bulk oxidation, findings which are important for developing an improved understanding of metallic oxidation and corrosion.

4.2 Atomic Oxygen Interactions with Clean and Adsorbate Covered Metallic Surfaces

One of the goals of modern surface science is to understand at the most fundamental level how oxygen interacts with metallic surfaces. This topic is of great technological importance due to the central role that oxygen-surface interactions have in determining the atomic-level mechanisms of such phenomena as metallic oxidation, corrosion, and chemical catalysis. To date, activity in this area of investigation has primarily concentrated on the interactions that molecular oxygen in its ground-electronic-state has with surfaces. In our group we have initiated ultra-high vacuum gas-surface scattering experiments in which a beam of atomic oxygen interacts with the interface in question, in this instance Rh(111). We envision three general directions for these studies: (i) to examine oxygen-metal surface chemistry in which the constraint of starting with a molecular rather than an atomic oxidant has been lifted, (ii) to elucidate whether differences exist in the rate of oxygen incorporation into the bulk depending on the nature of the oxidant, with concomitant consequences for metallic oxidation, and (iii) to explore the chemical reactivity of any new oxygen overlayer structures which form as a result of using novel oxidants.

Work with our first generation atomic oxygen beam source has been completed, and two second generation RF plasma atomic oxygen beam sources have been assembled. These new sources are capable of generating very intense beams of kinetic-energy-selected oxidants, such as  $O(^3P)$ ,  $O(^1D)$ , and  $O_2(^1\Delta)$ .

Paper #8. High Density Adsorbed Oxygen on Rh(111) and Enhanced Routes to Metallic Oxidation Using Atomic Oxygen, K. D. Gibson, Mark Viste, Errol C. Sanchez, and S. J. Sibener, J. Chem. Phys. (Communication) 110, 2757 (1999).

Exposure of Rh(111) to atomic oxygen leads to the facile formation of a full-coverage and ordered (1x1)-O monolayer which is stable at room temperature. This result differs markedly from the half-coverage (2x1)-O overlayer which forms at saturation when using molecular oxygen. This demonstrates that kinetic rather than thermodynamic constraints inhibit the formation of dense oxygen overlayers when O<sub>2</sub> is the oxidant. We also report that O absorption into the bulk proceeds much more readily when using O rather than O<sub>2</sub>, a finding with direct implications for enhanced methods of low-temperature metallic oxidation. These results demonstrate that there are important fundamental differences in the way in which low-energy beams of atomic and molecular oxygen interact with metals.

Paper #9. Physical and Chemical Properties of High-Density Atomic Oxygen Overlayers Under UHV Conditions: (1x1)-O/Rh(111), K.D. Gibson, M. Viste, E.C. Sanchez, and S.J. Sibener, J. Chem. Phys. 112, 2470 (2000). In this paper, we elaborate on our previous communication of high coverages of oxygen on Rh(111) (J. Chem. Phys. 110, 2757 (1999)). When dosing with  $O_2$ , half of a monolayer of O is adsorbed. Higher coverages can be achieved when exposing the surface to O atoms. As the quantity of adsorbed O increases from a half to a full monolayer, the overlayer structure undergoes several distinct phase changes. At a full monolayer, the (1x1)-O structure is stable at surface temperatures less than ~400 K. Continued dosing with O atoms results in the rapid migration of O into the bulk. We also report on the chemical reactivity of this densely oxygen-covered surface with CO, CO, and propene.

Paper #11. Enhanced Oxidation Rate of Ni(111) by Atomic Oxygen, J.A. Slezak, B.D. Zion, and S.J. Sibener, Surf. Sci. Lett. 442, L983-988 (1999). The oxidation of the Ni(111) surface by a supersonic atomic oxygen beam has been quantitatively studied using in situ high-resolution electron-energy-loss spectroscopy. For a room temperature substrate, a drastically different oxidation rate for atomic oxygen induced oxidation than for molecular oxygen based oxidation is observed. This rate was found to be two orders of magnitude higher than that of molecular oxygen. The reaction on a 110 K substrate

indicated oxygen uptake only to the chemisorption saturate with no further oxidation. This later finding agrees with previous results for low surface temperature oxidation using molecular oxygen, implying that the inhibiting step in low temperature Ni oxidation is not molecular oxygen dissociation, but a more fundamental property of the metallic substrate. The chemisorption region of the atomic oxygen reaction was found to saturate at the same (2x2) overlayer as results from exposure to molecular oxygen, i.e., a dense (1x1) overlayer as has been seen on other metals does not form on Ni(111).

4.3 Metallic Oxidation Using Energetic Oxidants: High Kinetic Energy Molecular Oxygen

Ben Zion, Aubrey Hanbicki, and Julie Slezak have explored kinetic energy effects in metallic oxidation. We have quantitatively examined the oxidation kinetics of the Ni(111) surface utilizing kinetic energy selected supersonic beams of molecular oxygen. Using in situ high-resolution electron-energy-loss spectroscopy, we have observed notable differences in the oxidation mechanism for this interface as a function of incident beam kinetic energy. Exposure of a 300 K surface to a relatively low energy 60 meV O<sub>2</sub> beam leads to oxidation kinetics which follow an island growth model, qualitatively similar to what is seen with simple ambient gas dosing. In contrast to this, exposure to a relatively high energy 600 meV O<sub>2</sub> beam yielded fundamentally different oxidation behavior: the kinetics of oxidation no longer follow an island growth model but rather behave with a Langmuir-like sticking model, implying key differences in the nucleation stage for interface oxidation. Cryogenically cooled Ni(111) could not be oxidized using either of these incident beam conditions, indicating that the energetic constraints needed to move from oxygen chemisorption to actual metallic oxidation cannot be simply overcome using incident O<sub>2</sub> kinetic energy.

Paper #7. Kinetic Energy Effects on the Oxidation of Ni(111) Using  $O_2$  Molecular Beams, B. D. Zion, A. T. Hanbicki, and S. J. Sibener, Surf. Sci. Letters  $\underline{417}$ , L1154-L1159 (1998).

The oxidation kinetics of the Ni(111) surface have been quantitatively examined utilizing kinetic energy selected supersonic beams of molecular oxygen. Using in situ high-resolution electron-energy-loss spectroscopy, we have observed notable differences in the oxidation mechanism for this interface as a function of incident beam kinetic energy. Exposure of a 300 K surface to a relatively low energy 60 meV O<sub>2</sub> beam leads to oxidation kinetics which follow an island growth model, qualitatively similar to what is seen with simple ambient gas dosing. In contrast to this, exposure to a relatively high energy 600 meV O<sub>2</sub> beam yielded fundamentally different oxidation behavior: the kinetics of oxidation no longer follow an island growth model but rather behave with a Langmuir-like sticking model, implying key differences in the nucleation stage for interface oxidation. Cryogenically cooled Ni(111) could not be oxidized using either of these incident beam conditions, indicating that the energetic constraints needed to move from oxygen chemisorption to actual metallic oxidation cannot be simply overcome using incident O<sub>2</sub> kinetic energy.

4.4 Influence of Surface Stress in Oxidation/Corrosion Chemistry of Al, Al-2024-T3, NiAl

During the past few years we have refined our capability to examine the reactivity of metals in the presence of an externally applied stress field, and can now conduct such atomic force microscopy based measurements, as a function of tensile or compressive stress, systematically spanning the range from no stress up to the yield strength for a given material. Our work has included (i) electrochemical corrosion of Al 2024-T3 and pure Ni, (ii) pitting corrosion for pure polycrystalline Al using *in situ* scanning probe microscopy, and, most recently, (iii) corrosive reactions in liquid environments leading to etch pit formation and real-time studies of metallic grain dissolution. Related work on single crystals of Al and NiAl has also been initiated.

We have succeeded, unambiguously, in demonstrating that externally applied stresses can influence the electrochemical corrosion of metals. Specifically, the electrochemical corrosion of aluminum 2024-T3 and of pure nickel were explored by anodizing metal surfaces under stress. Statistical analyses of AFM images yields information on etch pit size and shape distributions produced under compressive and tensile stress. Etch pits created under tensile stress are bigger, deeper and denser than those formed under compressive stress. This effect is systematically enhanced as the amount of applied stress is increased. Etch pit morphologies are also being examined with AFM.

The basic science opportunities addressed in this effort are quite significant. Surface stress has recently been discussed as a key parameter in surface reactivity, but definitive measurements are lacking. Such effects due to stress are not unexpected given the observation that structural relaxation and surface stress field changes frequently accompany adsorption, especially including oxygen adsorption on metallic interfaces. We are in some sense turning this question around, seeing if we can influence surface oxidative chemistry by tuning the level of stress, including both compressive and tensile regimes. This issue is of particular interest in the vicinity of load levels which lead to surface reconstruction and crystal facetting.

Paper #19. Stress Effects in the Electrochemical Pitting Corrosion of Aluminum 2024-T3 and Pure Nickel Using Atomic Force Microscopy, Applied Surf. Sci., 161, 375-384 (2000).

In this paper we demonstrate that externally applied tensile and compressive stresses can systematically modify the electrochemical surface reactivity of pure and alloyed metals. Atomic force microscopy is used to statistically characterize the extent and nature of interface change for nickel and aluminum alloy 2024-T3 subjected to electrochemical conditions under various levels of stress. Statistical analysis of AFM images reveals that the extent of electrochemical reactivity is significantly enhanced when subjecting the sample to tensile as opposed to compressive stress; this enhancement increases monotonically as the level of applied stress is systematically increased. Surface morphologies differ on the pure nickel and alloyed aluminum samples, with the nickel interfaces exhibiting facetted features which are aligned 120° from one another while the surface features on aluminum alloy 2024-T3 are circular pores. These results unambiguously indicate that the kinetics for electrochemical metallic processes, which nucleate at surface defects and grain boundaries, can be significantly modified by the presence of external stress fields.

## 4.5 Formation of High-Density and Highly-Ordered Water Layers on (1x1)-O-Rh(111)

We have discovered that when water adsorbs on the high-density (1x1) oxygen overlayer that it forms a very unusual structure which is related to ice structures that normally form at extraordinarily high pressures (20Kbar or higher). This "templating effect" of the chemisorbed oxygen overlayer also causes a reversal in the orientation of hydrogen-bonds between the first water layer and the substrate, with hydrogen atoms pointing down. These findings may have ramifications for the chemistry which occurs near oxygen covered surfaces which are covered with water, as well as for reactions occurring in liquid environments. These results come from He diffraction data which are sensitive hydrogen and oxygen atoms, a situation which differs from typical LEED and x-ray data. Our data set now encompasses bilayer and multilayer water structures on clean and oxygen covered metallic surfaces.

Paper #16. The Adsorption of Water on Clean and Oxygen Pre-Dosed Rh(111): Surface Templating via (1x1)-O/Rh(111) Induces Formation of a Novel High-Density Ice Structure, K.D. Gibson, M. Viste, and S.J. Sibener, J. Chem. Phys. 112, 9582-9589 (2000).

Water adsorbed on clean Rh(111) forms an ordered structure with a  $(\sqrt{3} \text{ x} \sqrt{3})\text{R}30^{\circ}$  diffraction pattern. This is facilitated by the close match of surface lattice constants for Rh(111) and the (0001) face of hexagonal ice, Ih. The pre-adsorption of small quantities of disordered oxygen improves the long-range ordering of the water overlayer. When a well-ordered half monolayer of oxygen is grown on the Rh(111) prior to H2O exposure, there is no evidence of any longrange ordering of the water. However, when  $\bar{H}_2O$  is adsorbed on a (1x1)-O/Rh(111) surface, where there is a well-ordered monolayer of adsorbed oxygen, the adsorbed H<sub>2</sub>O forms a new high-density structure exhibiting a (1x1) diffraction pattern. The adsorbed  $H_2O$  structure is epitaxial with respect to the underlying oxygen and rhodium. This structure persists for many layers of adsorbed water. On the clean Rh(111) surface, water molecules are adsorbed through the oxygen lone pair orbital. When the surface is fully covered with oxygen, the first layer of water can hydrogen bond to the surface, i. e., they likely adsorb with one or both of the hydrogen atoms pointing towards the surface. This creates a template for a novel structure which forms at low pressure, producing a high-density crystalline form of interfacial ice. This discovery suggests that other molecules, especially those that hydrogen bond, may form new structures on metals covered with a high-density oxygen overlayer, with associated consequences for interfacial chemistry.

## 4.6 The Effect of Cluster Formation on Mass Separation in Binary Molecular Beams

Supersonic molecular beam techniques are widely used in the study of gas-phase and gas-surface collision phenomena. In many applications, one uses mixed, i.e. seeded, beams to accelerate or decelerate a species in order to tune its energy over a rather wide range. It has been well documented that a variety of factors contribute to mass separation in such skimmed and seeded beams, which can lead to substantial differences between the starting composition of the expansion gas and the characteristic of the downstream sampled beam. This composition distortion becomes of crucial concern whenever a quantitative measurement is needed. Much effort has been made to understand and quantify such mass separation phenomena which arise during expansion. Unfortunately, some confusion still exists due to the complexity of the problem, as well as the variation of measurement configurations used in these studies.

In our group have examinined the composition changes which arise for an anti-seeded binary mixture, in which the minority species is lighter than the carrier gas. In particular, we have examined the downstream depletion of the seed gas as a function of stagnation pressure and nozzle temperature. Neon/xenon and oxygen/xenon mixtures were used in these studies. Strong evidence has been found which implicates cluster formation in the heavier carrier gas as inducing downstream seed gas depletion which exceeds the levels commonly seen. Existing theories of mass separation in binary supersonic flows do not adequately account for this striking phenomenon. These effects are not small, with light/heavy composition ratios in the downstream flows decreasing by an order of magnitude as referenced to the initial composition of the gas before supersonic expansion and skimmer sampling. It is our belief that these findings will lead to refinements in our ability to predict the dynamic behavior of high-Mach number gas flows. There may also be significant ramifications for new methods of hydrodynamic isotope separation.

Paper #15. The Effect of Cluster Formation on Mass Separation in Binary Molecular Beams, Wei Li, M.J. Stirniman, and S.J. Sibener, J. Chem. Phys. 112, 3208-3213 (2000).

The downstream composition of a skimmed supersonic binary molecular beam originally consisting of a 20% neon/80% xenon mixture before expansion has been studied as a function of nozzle stagnation pressure. We have found that the neon to xenon ratio dropped dramatically as the stagnation pressure was increased at low nozzle temperature (303 K), a drop which cannot be well described by existing theory. Time-of-flight (TOF) measurements indicate that Xe

clustering occurs as the stagnation pressure is increased. This clustering coincides with the additional Ne depletion we observe. At a higher nozzle temperature where Xe clustering does not occur (573 K), this measured mass separation phenomenon is absent. Similar experiments have been done for another binary mixture,  $20\% \ O_2/80\%$  Xe. Similar anomalous mass separation is observed with this mixture, confirming the attribution of this phenomenon to clustering of the more massive component of the mixture. These findings have implications for novel methods of gas-dynamics-based mass separation potentially including isotope enrichment.

4.7 Adsorbates on Stepped/Kinked Metallic Interfaces - Nanostructures
Stepped (vicinal) single crystal surfaces are very informative model systems for probing the chemical, physical, and metallurgical properties of imperfect surfaces. They also provide a superb platform for creating self-organizing nanostructures. Careful preparation of such surfaces allows one to produce samples having known crystallographic orientation and hence controlled numbers and types of interfacial defects. We have examined the behavior of hydrogen and Xe adsorbed on such surfaces. Our work on atomically templated Xe was the Cover Story of a recent issue of J. Phys. Chem. B.

Paper #12. Rational Design of Interfacial Structure: Adsorbate-Mediated Templating, S.B. Darling, A.T. Hanbicki, T.P. Pearl, and S.J. Sibener, J. Phys. Chem. B 103, 9805-9808 (1999).

In this letter we show that it is possible to guide the formation of a novel non-close-packed xenon structure on a stepped nickel surface using an intentionally atomically-patterned substrate. By first defining the symmetry and desired dimensions of the underlying superlattice, we successfully template the targeted rare gas overlayer. Such templating effects, in which the corrugation and structure of the interface can be tuned by prior adsorption of an adsorbate, should be a general route to the formation of new self-organizing interfacial nanoscale structures.

Paper #14. Influence of Steps on the Interaction Between Adsorbed Hydrogen Atoms and a Nickel Surface, Aubrey T. Hanbicki, S.B. Darling, D.J. Gaspar, and S.J. Sibener, J. Chem. Phys. 111, 9053-9057 (1999).

In this paper we demonstrate that externally applied tensile and compressive stresses can systematically modify the electrochemical surface reactivity of pure and alloyed metals. Atomic force microscopy is used to statistically characterize the extent and nature of interface change for nickel and aluminum alloy 2024-T3 subjected to electrochemical conditions under various levels of stress. Statistical analysis of AFM images reveals that the extent of electrochemical reactivity is significantly enhanced when subjecting the sample to tensile as opposed to compressive stress; this enhancement increases monotonically as the level of applied stress is systematically increased. Surface morphologies differ on the pure nickel and alloyed aluminum samples, with the nickel interfaces exhibiting facetted features which are aligned 120° from one another while the surface features on aluminum alloy 2024-T3 are circular pores. These results unambiguously indicate that the kinetics for electrochemical metallic processes, which nucleate at surface defects and grain boundaries, can be significantly modified by the presence of external stress fields.

4.8 Polymer Thin Film Coatings

We have performed the first measurements of how individual defects in cylinder-forming diblock copolymers move and topologically evolve, including defect annihilation events, during polymer annealing. This has been accomplished for cylinder-forming polystyrene-block-polymethylmethacrylate films using atomic force microscopy. Such processes form the basis for predicting structural change in polymer films. This work has most recently focussed on devising new routes to forming oriented thin polymer film structures.

Paper #4. Silicon Nitride Membrane Substrates for the Investigation of Local Structure in Polymer Thin Films, T.L. Morkved, W.A. Lopes, J. Hahm, S.J. Sibener, and H.M. Jaeger, Polymer (Communication) 39, 3871 (1998).

We describe the fabrication of silicon nitride membrane substrates and their use in studies of polymer thin films. As an integral part of a wafer, these membranes are both self-supporting and transparent for transmission electron microscopy (TEM). Therefore, the same polymer film can be spin-cast on the substrate and, without being removed, studied by a variety of techniques, including TEM, and atomic force microscopy (AFM). To demonstrate the utility of these substrates in characterizing both global and local film morphology, we present experimental results on polystyrene-polymethylmethacrylate diblock copolymers in the ultrathin film limit, using optical microscopy together with combinations of AFM and TEM at the same location. We also discuss the addition of microfabricated structures to these substrates, such as planar electrodes.

Paper #6. Defect Evolution in Ultrathin Films of Polystyrene-block-Polymethylmethacrylate Diblock Copolymers Observed Using Atomic Force Microscopy, J. Hahm, W. A. Lopes, H. M. Jaeger, and S. J. Sibener, J. Chem. Physics (Communication) 109, 10111-10114 (1998).

We track individual defects in the microdomain patterns of cylinder-forming polystyrene-block-polymethylmethacrylate films with atomic force microscopy to elucidate the evolution of diblock domain topology during annealing. This evolution takes place through relinking, joining, clustering, and annihilation of defects. Such processes form the basis for predicting structural change in polymer films.

Paper #18. Cylinder Alignment in Annular Structures of Microphase Separated Polystyrene-B-Polymethylmethacrylate, J. Hahm and S. J. Sibener, Langmuir 16, 4766-4769 (2000).

We present a novel and simple method for generating micron-scale annular structures formed from polystyrene-b-polymethylmethacrylate (PS-b-PMMA) diblock copolymer on a silicon oxide substrate. This method is based on pre-wetting of the underlying substrate with a minor polar solvent before spin-casting of the diblock solution. When using this procedure we also see, using atomic force microscopy, a unique alignment effect which occurs in the cylinder-forming microdomains of PS-b-PMMA annuli without the aid of an external alignment field. These aligned microdomains, with controlled nanometer-scale spacing and coherence on the order of microns, facilitate the ongoing exploration of self-organizing nanofabricated surfaces.

4.9 Multiphonon Energy Transfer in Gas-Surface Collisions

We have completed a study of how energy is transferred to a stepped surface due to gas-surface collisions. Such information is not only of fundamental interest, but also gives insight into airframe heating during high-velocity flight. Specifically, the multiphonon energy exchange between a neutral He atom and a stepped Ni(977) surface was measured in order to examine how the presence of a regular array of atomic-scale steps on a surface modifies energy exchange in the classical multiphonon scattering regime. At elevated substrate temperatures, we compared the multiphonon scattering with the predictions of a classical theory that has previously been used by others for assessing energy exchange involving a smooth surface. There is a significant discrepancy between the theoretical predictions and our experimental data, which we attribute to differences between a smooth and stepped surface. Specifically, changes in the vibrational modes and associated surface density of states due to the presence of extended surface defects have a fundamental impact on the details of the energy exchange mechanism.

Paper #5. Inelastic Multiphonon Helium Scattering from a Stepped Ni(977) Surface, Daniel J. Gaspar, Aubrey T. Hanbicki, and S. J. Sibener, J. Chem. Phys. 109, 6947-6955 (1998).

The multiphonon energy exchange between a neutral He atom and a stepped Ni(977) surface has been measured in order to examine how the presence of a regular array of atomic-scale steps on a surface modifies energy exchange in the classical multiphonon scattering regime. At elevated substrate temperatures, we compare the multiphonon scattering with the predictions of a classical theory that has previously been used by others for assessing energy exchange involving a smooth surface. There is a significant discrepancy between the theoretical predictions and our experimental data, which we attribute to differences between a smooth and stepped surface. Specifically, changes in the vibrational modes and associated surface density of states due to the presence of extended surface defects have a fundamental impact on the details of the energy exchange mechanism.

4.10 Surface Ordering Kinetics of Metallic Alloys

We are continuing our examination of the chemical and physical properties of metallic alloy surfaces. Such studies are important to the design of material interfaces which maintain good structural properties in corrosive and especially high temperature environments. Samples consisting of both ordered and disordered regions are of further interest, as their physical properties, such as resistance to dislocation propagation and brittleness, can be optimized for a specific application given our present understanding of the relationship between microstructure and micromechanics. For this reason 'superalloys' are currently used in high performance applications of the aerospace industry. These alloys exhibit increased hardness in their ordered phase as compared to their disordered phase or their single metal constituents.

In our group we have initially focussed on the model system Cu<sub>3</sub>Au(001), with two of the primary goals being to investigate how interatomic forces differ between the surface and bulk regions of an intermetallic compound, and how the surface structure changes in the vicinity of the disordering temperature of the alloy -- ideally revealing how the ordered and substitutionally disordered surface domains evolve as a function of temperature. The phonon work on the ordered phase is complete and has been published. To summarize, the experimentally measured dispersion curves do not agree with those generated by a lattice dynamical slab calculation which uses a pair potential force-field that successfully models the bulk vibrations of the ordered alloy. The best fit to our experimental data indicates that the force constant between the first and second layer Cu atoms needs to be stiffened by 20% with respect to the bulk value.

Our main focus is presently on structural and dynamical issues at elevated temperatures in the vicinity of the bulk critical temperature, 664 K. We have seen that the surface begins to disorder at temperatures well below the bulk T<sub>c</sub>, in agreement with previous LEED studies on this interface. We have now conducted kinetic measurements in an attempt to observe in real time how the surface orders following quenching from above Tc to temperatures below Tc. Our preliminary results have revealed for shallow temperature quenches that the surface orders much more rapidly than the bulk, while for deeper quenches the surface ordering rate is quite comparable to that found in x-ray studies of the bulk. Such dynamical measurements reveal important details about the approach to equilibrium, i.e., how quenched systems evolve through the various stages of nucleation, ordering, and coarsening. We are also probing whether the temperature history of the quenched sample can influence how order is first established in the alloy, i.e., originating at the surface and propagating into the bulk (with the surface acting as a template) or whether order originates throughout the bulk of the sample. Such issues may ultimately influence the microstructure, and hence micromechanics, of the alloy. Anharmonic effects in the surface phonon spectrum of this surface have been observed approximately 20 degrees below the bulk T<sub>c</sub>, an increase which we attribute to the onset of anharmonic effects in the phonon dynamics. Note that this onset coincides with the beginning of surface disordering for this alloy. Related anharmonic effects have been observed just below Tc for the bulk using neutron scattering as the dynamical probe.

This work is still in progress; manuscript(s) will be submitted at a later date.

4.11 Surface Chemistry

This grant has also partially supported various projects in surface chemical dynamics. Papers 2, 3, 10, and 17 (see below) cover these activities.

Paper #2. Dynamics of NO Reduction by H<sub>2</sub> on Rh(111): Velocity and Angular Distributions of the N<sub>2</sub> Product, J.I. Colonell, K.D. Gibson, and S.J. Sibener, J. Chem. Phys. <u>104</u>, 6822 (1996).

The velocity and angular distributions of N<sub>2</sub> produced from the reduction of NO by H<sub>2</sub> on Rh(111) have been measured in the low nitrogen coverage limit as a function of surface temperature. Both the angular and velocity distributions are well fit by bimodal forms. The high energy channel has average translational energies about six times that expected for molecules accommodated at the surface temperature, an unusually sharp angular distribution and angle dependent velocity distributions. The low energy channel is also hyperthermal, with average translational energies about twice thermal, a cosine angular distribution, and velocity distributions which are independent of angle. Application of surprisal analysis to the data shows that the high energy channel may be characterized by constraints on the normal velocity and the total energy; the low energy channel may be characterized by a single constraint on the velocity.

Paper #3. Coverage Dependence of the Kinetics for H<sub>2</sub> Desorption from Rh(111), J.I. Colonell, T.J. Curtiss, and S.J. Sibener, Surf. Sci. <u>366</u>, 19 (1996).

Coverage dependent sticking probabilities and second order rate constants for recombinative desorption of hydrogen from Rh(111) have been measured using molecular beam relaxation spectroscopy (MBRS) and time-resolved specular helium scattering. The sticking probability follows second order Langmuir coverage dependence with  $s_0$  equal to  $0.01 \pm .005$ . Under isothermal and nearly isosteric conditions over the coverage range 0.2 ML to 0.7 ML, the second order rate constant for desorption is essentially independent of hydrogen coverage, in contrast to kinetic parameters determined from thermal desorption spectra.

Paper #10. The Decomposition of NO<sub>2</sub> On Rh(111): Product NO Velocity And Angular Intensity Distributions, K.D. Gibson, J.I. Colonell, and S.J. Sibener, Surf. Sci. 443, 125-132 (1999).

The velocity and angular distributions of NO produced from the decomposition of  $NO_2$  on Rh(111) under both reducing and oxidizing conditions have been measured at surface temperatures between 500 K and 1000 K. When a concurrent  $H_2$  beam is used, which keeps the surface free of oxygen, the NO product has much more translational energy than expected for equilibration at the surface temperature, but is dependent on  $T_s$ . There is total energy scaling; the translational energy is independent of final angle. A small amount of  $N_2$  is also produced. When the  $H_2$  beam is turned off, oxygen builds up on the surface. Under this oxidizing condition, the NO product has a nearly Maxwell-Boltzmann velocity distribution at the surface temperature.

Paper #17. Heterogeneous Combustion of Benzene on Rh(111): Kinetics and Dynamics of CO And CO<sub>2</sub> Production, M.E. Viste, K.D. Gibson, and S.J. Sibener, J. of Catalysis, 191, 237-244 (2000).

The heterogeneous combustion of benzene on Rh(111) has been examined using molecular beams in an ultra-high vacuum environment. For the reaction conditions studied, CO is the dominant carbon-containing product.  $CO_2$  is a minor component, accounting for a maximum of 10% of the carbon species at 650 K and dropping to 2% when the temperature is raised to 1000 K. The relative yields of CO and  $CO_2$ , as well as the reaction rate for CO production, are strongly influenced by surface oxygen concentration, controlled though the relative ratio of

oxygen and benzene fluxes, with the fastest rate of CO production and the greatest proportion of  $CO_2$  occurring under the most oxidizing conditions. Because the catalytic decomposition of benzene is rapid on the rhodium surface, the kinetics of CO and  $CO_2$  evolution are dominated by the reaction of atomic carbon and oxygen species on the surface. We calculate an activation energy for the reaction  $C(a) + O(a) \rightarrow CO(a)$  of 130 kJ/mol.  $CO_2$  is produced by the further reaction of CO with adsorbed O, with the extent of reaction being substantially influenced by reaction at defect sites. CO is evolved with a thermal kinetic energy distribution, while  $CO_2$  desorbs hyperthermally.

5. Personnel Supported and Associated with This Program

Our research program has been quite successful in attracting and educating some of the best young scientific talent in the country, including undergraduates, graduate students, and postdoctoral fellows.

Personnel (PD: Postdoctoral Fellow; GS: Graduate Student, UG: Undergraduate):

Steven J. Sibener, Professor and PI

Kevin Gibson (Research Scientist, U. of Chicago)

Aubrey Hanbicki (Research Associate, U. of Chicago; now at NRL)

Daniel Gaspar (GS, U. of Chicago; graduated with Ph.D. August 1998; now at DOE-PNNL)

Mark Viste (GS, U. of Chicago; graduated with Ph.D. June 1999; now at Medtronics Corp.)

Ben Zion (GS, U. of Chicago)

Julie Slezak (GS, U. of Chicago)

Bill Isa (GS, U. of Chicago)

Tom Pearl (GS, U. of Chicago; graduated with Ph.D. August 2000; now at Penn State Univ)

Jongin Hahm (GS, U. of Chicago; graduated with Ph.D. June 2000; now at Harvard)

Shoshana Gourdin (UG, U. of Chicago)

Patrick Yu (UG, U. of Chicago)

Claire Jacobs (UG, U. of Chicago)

## Recent Alumni Who Have Contributed to AFOSR Sponsored Projects:

[\*\* Indicates alumni who have contributed to this AFOSR program during the past grant period.]

Gillian Zacharias\*\* (UG, B.S. 6/98; now at U. Iowa)

Errol Sanchez\*\* (GS, Ph.D. 3/97; posdoc at U. of Colorado at Boulder; now at Applied Materials)

Wei Li\*\* (PD, U. of Chicago; formerly at Intel, now at Lucent Technologies)

Michael Stirniman\*\* (GS, U. of Chicago; formerly at Battelle PNNL as Postdoc, now at Seagate)

Licheng Niu\*\* (GS, Ph.D. Dec 1994; now at Applied Materials)

Suzanne King (GS, Ph.D. March 1993; now at US-EPA)

Daniel Koleske (GS, Ph.D. Dec. 1991; now at NRL following IBM postdoc)

Eric Bittner (GS, Ph.D. Aug.1994; UC advisor John Light; now faculty at U. of Houston)

6. Publications Resulting from this Grant (1996-2000)

- 1. Reconstruction Kinetics of a Stepped Metallic Surface: Step Doubling and Singling of Ni(977) Induced by Low Oxygen Coverage, L. Niu, D. D. Koleske, D. J. Gaspar, S. F. King and S. J. Sibener, Surf. Sci. <u>356</u>, 144 (1996).
- 2. Dynamics of NO Reduction by H<sub>2</sub> on Rh(111): Velocity and Angular Distributions of the N<sub>2</sub> Product, J.I. Colonell, K.D. Gibson, and S.J. Sibener, J. Chem. Phys. <u>104</u>, 6822 (1996).
- 3. Coverage Dependence of the Kinetics for H<sub>2</sub> Desorption from Rh(111), J.I. Colonell, T.J. Curtiss, and S.J. Sibener, Surf. Sci. <u>366</u>, 19 (1996).

- 4. Silicon Nitride Membrane Substrates for the Investigation of Local Structure in Polymer Thin Films, T.L. Morkved, W.A. Lopes, J. Hahm, S.J. Sibener, and H.M. Jaeger, Polymer (Communication) 39, 3871 (1998).
- 5. Inelastic Multiphonon Helium Scattering from a Stepped Ni(977) Surface, Daniel J. Gaspar, Aubrey T. Hanbicki, and S. J. Sibener, J. Chem. Phys. <u>109</u>, 6947-6955 (1998).
- 6. Defect Evolution in Ultrathin Films of Polystyrene-block-Polymethylmethacrylate Diblock Copolymers Observed Using Atomic Force Microscopy, J. Hahm, W. A. Lopes, H. M. Jaeger, and S. J. Sibener, J. Chem. Physics (Communication) 109, 10111-10114 (1998).
- 7. Kinetic Energy Effects on the Oxidation of Ni(111) Using O<sub>2</sub> Molecular Beams, B. D. Zion, A. T. Hanbicki, and S. J. Sibener, Surf. Sci. Letters <u>417</u>, L1154-L1159 (1998).
- 8. High Density Adsorbed Oxygen on Rh(111) and Enhanced Routes to Metallic Oxidation Using Atomic Oxygen, K. D. Gibson, Mark Viste, Errol C. Sanchez, and S. J. Sibener, J. Chem. Phys. (Communication) 110, 2757 (1999).
- 9. Physical and Chemical Properties of High-Density Atomic Oxygen Overlayers Under UHV Conditions: (1x1)-O/Rh(111), K.D. Gibson, M. Viste, E.C. Sanchez, and S.J. Sibener, J. Chem. Phys. <u>112</u>, 2470 (2000).
- 10. The Decomposition of NO<sub>2</sub> On Rh(111): Product NO Velocity And Angular Intensity Distributions, K.D. Gibson, J.I. Colonell, and S.J. Sibener, Surf. Sci. <u>443</u>, 125-132 (1999).
- 11. Enhanced Oxidation Rate of Ni(111) by Atomic Oxygen, J.A. Slezak, B.D. Zion, and S.J. Sibener, Surf. Sci. Lett. 442, L983-988 (1999).
- 12. Rational Design of Interfacial Structure: Adsorbate-Mediated Templating, S.B. Darling, A.T. Hanbicki, T.P. Pearl, and S.J. Sibener, J. Phys. Chem. B <u>103</u>, 9805-9808 (1999).
- 13. Proximity Heater for the Elevated Temperature *In Situ* Vacuum Scanning Tunneling Microscopy of Metal Surfaces, T.P. Pearl and S.J. Sibener, Rev. Sci. Instrum. <u>71</u>, 124-127 (2000).
- 14. Influence of Steps on the Interaction Between Adsorbed Hydrogen Atoms and a Nickel Surface, Aubrey T. Hanbicki, S.B. Darling, D.J. Gaspar, and S.J. Sibener, J. Chem. Phys. <u>111</u>, 9053-9057 (1999).
- 15. The Effect of Cluster Formation on Mass Separation in Binary Molecular Beams, Wei Li, M.J. Stirniman, and S.J. Sibener, J. Chem. Phys. <u>112</u>, 3208-3213 (2000).
- 16. The Adsorption of Water on Clean and Oxygen Pre-Dosed Rh(111): Surface Templating via (1x1)-O/Rh(111) Induces Formation of a Novel High-Density Ice Structure, K.D. Gibson, M. Viste, and S.J. Sibener, J. Chem. Phys. 112, 9582-9589 (2000).
- 17. Heterogeneous Combustion of Benzene on Rh(111): Kinetics and Dynamics of CO And CO<sub>2</sub> Production, M.E. Viste, K.D. Gibson, and S.J. Sibener, J. of Catalysis, <u>191</u>, 237-244 (2000).
- 18. Cylinder Alignment in Annular Structures of Microphase Separated Polystyrene-B-Polymethylmethacrylate, J. Hahm and S. J. Sibener, Langmuir <u>16</u>, 4766-4769 (2000).

19. Stress Effects in the Electrochemical Pitting Corrosion of Aluminum 2024-T3 and Pure Nickel Using Atomic Force Microscopy, Applied Surf. Sci., <u>161</u>, 375-384 (2000).

7. Interactions/Transitions

7a. Invited Presentations of the PI

1996

UCLA, Department of Chemistry, Los Angeles, CA

Univ. of Penn., Department of Chemistry, Philadelphia, PA

DARPA Meeting on Chemical Corrosion and Coatings, San Diego, CA

Modern Trends in Chemical Dynamics - 60th Birthday Fest for Yuan T. Lee,

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, R.O.C. (Dec. 1996).

1997

Univ. of Utah, Department of Chemistry, Salt Lake City, UT

March Meeting of the APS, Kansas City, KS

U. of Chicago/Argonne Natl. Lab Meeting on Collaborative Research, Oakbrook, IL

1997 Conference on the Dynamics of Molecular Collisions, Gull Lake, MN

Gordon Research Conference on Dynamics of Gas-Surface Interactions, Andover, NH

DARPA/AFOSR Conference on Aircraft Coatings and Corrosion, Annapolis, MD

1998

National ACS Meeting (March 1998), Dallas, Texas; Symposium on Interfacial Water

National ACS Meeting (August 1998), Boston, MA; Symposium on Structure and Electronic Properties of Materials by Scanning Probe Microscopy

DARPA/AFOSR Conference on Aircraft Coatings and Corrosion, Annapolis, MD

1999

Univ. of Illinois at Chicago, Department of Chemistry, Chicago, IL Wayne State University, Department of Chemistry, Detroit, MI Univ. of Pittsburgh, Department of Chemistry, Pittsburgh, PA

## 7b1. Connections with DoD

The PI and his group have attended several DoD meetings on the topic of corrosion and aging aircraft. For example:

• Graduate student Mike Stirniman participated in the "Joint AFOSR-AFMC/EN Aging Aircraft Conference" [Workshop on Aging Aircraft Research] that was held from 27-28 April

1993 at Georgia Tech in Atlanta, GA.

• Professor Sibener was an invited participant at the "Second Air Force Aging Aircraft Conference" that was held from 17 May to 19 May at the Oklahoma City Air Logistics Center, Tinker AFB, OK. His talk was entitled "The Initial Stages of Metallic Oxidation", and stimulated much discussion with the participants and sponsors.

• Professor Sibener was also an invited speaker at the AFOSR/URI Meeting on "Corrosion, Tribology, Lubrication, and Materials Fatigue Under Extreme Conditions" that was held from 17-18 August 1994 at the Beckman Institute at the Univ. of Illinois/Urbana-Champaign. His presentation was entitled "The Initial Stages of Metallic Oxidation", and was presented at a much higher technical level than the overview talk presented earlier at Tinker AFB.

• Professor Sibener was an invited speaker at the DARPA Meeting on Chemical Corrosion

and Coatings, November 19-21, 1996 in San Diego, CA

• Professor Sibener was an invited speaker at the DARPA/AFOSR Conference on Aircraft

Coatings and Corrosion, September 15-18, 1997 in Annapolis, MD

• Professor Sibener was an invited speaker at the DARPA/AFOSR Conference on Aircraft Coatings and Corrosion, September 28, 1998 in Annapolis, MD

7b2. DoD Consulting of the PI

The PI was a charter member of the Defense Science Study Group of the Institute for Defense Analyses. He is currently a consultant for IDA.

7c. **Transitions** 

Electronics for High-Impedance STM Imaging 1. Title:

Circuitry needed for STM imaging of molecular overlayers Recipient: Mark Greenbaum, Topometrix Corporation (708-717-0566)

2. Title:

Ultra-High Vacuum Technology for Atomic Traps

Purpose:

Generation of ultra-low temperature atomic beams for

atomic/synchrotron physics and small-scale pattern deposition

Recipient: Bruce Zabransky, Argonne National Lab (630-252-4046)

## Section 7c Continues on the Next Page

3. Title:

Multiple Supersonic Molecular Beam Methods of Materials Growth

Improved growth of advanced semiconductors

Recipient: Dr. Hiroshi Kajiyama/Dr. Hrvoje Petek

Advanced Research Laboratory, Hitachi Ltd., Japan

4. Title:

Electron Enhanced Oxidation of Materials

Purpose: Improved oxidation and patterning of semiconductors

Recipient: Dr. Wilson Li, Intel Corp., (408-765-2837) [now at Lucent Technologies]

5. Title:

Technology for Generating Supersonic Molecular Beams

Intense sources of cooled atoms for synchrotron experiments in atomic physics

Recipient: Dr. Linda Young, Argonne National Laboratory, (630-252-8878)

6. Title:

Advanced Methods of Electron Stimulated Materials Oxidation

Improved oxidation, patterning, and passivation of materials

Recipient: Dr. Michael Stirniman, Seagate Technology (510-353-4935)

## 8. New Discoveries, Inventions, or Patent Disclosures

No Inventions or Patent Disclosures. Note that research on electron stimulated oxidation of materials and, perhaps, mass separation in supersonic flows may have follow-on applications.

#### 9. Honors/Awards

Elected Fellow, American Physical Society (November, 1997).

Appointed Director, Materials Research Science and Engineering Center (MRSEC) at The

University of Chicago, July 1997-.

Chairman, Div. of Chemical Physics, American Physical Society, 1996-97;

Chair-Elect (1995-96); Vice-Chair (1994-95).

Visiting Fellow, Joint Institute for Laboratory Astrophysics, Univ. of Colorado, Boulder, 1992-93.

Marlow Medal of the Faraday Division of the Royal Society of Chemistry, 1988.

Chairman, 1987 Gordon Conference on the Dynamics of Gas-Surface Interactions; Vice-Chair 1985.

Charter Member, Defense Science Study Group--Institute for Defense Analyses (1985-1988).

IBM Faculty Development Award, 1984-86.

Alfred P. Sloan Foundation Research Fellow, 1983-87.

Camille and Henry Dreyfus Young Faculty in Chemistry Award, 1980.

Gulf Oil Research Fellow, University of California, Berkeley, 1977.

American Institute of Chemists Award, University of Rochester, 1975.

Phi Beta Kappa, University of Rochester, 1975.